1346393

PATENT SPECIFICATION

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(19)

(54) MEANS FOR EFFECTING IMPROVEMENTS TO MASS SPECTROMETERS AND MASS FILTERS

(71) We, UNISEARCH LIMITED, a company limited by guarantee and incorporated under the laws of the State of New South Wales, Commonwealth of Australia, of University of New South Wales, Barker Street, Kensington, New South Wales, Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a mass spectrometer of the quadrupole type similar in operation to the mass filter described in the paper Paul W. and Raether M. "Das elektrisch Massenfilter", Zeit. Phys. Vol. 140, No. 3, May 1955, p. 262 the action of which was described by the Mathieu differential equation and which employed a focussing action on ions in flight through an electric field which was time-varying in a manner described by the Mathieu equation, the Mathieu equation being a particular form of the Hill equation. The operation of mass spectrometers according to the present invention is however based upon other forms of the Hill equation and employs analyzing electrode structures which include quadrupole and other configurations.

The mass spectrometers based upon the paper referred to above utilize a variety of analyzing electrode configurations, e.g. quadrupole cylindrical, monopole cylindrical, or hyperboloidal. The present invention also employs these electrode configurations which are the bases for mass spectrometers of the kinds known respectively as quadrupole mass spectrometers, monopole mass spectrometers, and three-dimensional rotationally symmetric ion cages, all of which can be said to function on the quadrupole principle, and which will be referred to compendiously in this specification as mass spectrometers of the quadrupole type. The authors referred to above and all subsequent workers have energised the analyzing electrodes of such mass spectrometers by an electric potential composed of a constant potential to which has been added a sinusoidally time-varying potential or by a plurality of sinusoidally time-varying potentials of discrete non-commensurate frequencies. It is to be noted that any references to electrodes in this specification are to be taken to be references to the analyzing electrodes of mass spectrometers as distinct from those other electrodes used to generate and detect ions. The analysis of ion flight through the electrode region has accordingly been carried out by ascertaining and making use of appropriate solutions of the Mathieu differential equation. Such mass spectrometers are described, *inter alia*, in United States of America Patent Specifications Nos. 2,939,952 and 2,950,389, in United States of America Patent Specification No. 3,129,327 and in United States of America Patent Specification No. 3,527,939.

The present invention contemplates the use of a similar variety of electrode configurations, the electrodes being energised by means arranged to generate the periodic time-varying electric potential which is defined below.

The analysis of ion flight through the electrode region is carried out by ascertaining and making use of appropriate solutions to the more general Hill differential equation rather than the Mathieu equation which is a particular case of the Hill equation.

Mass spectrometers according to the present invention have improved characteristics as compared with existing instruments which give rise to the following advantages:

1. Improved insensitivity of operation to variatiins of operating parameters and variables in the electronic control units of the spectrometers and filters, resulting in reduced complexity of electronic circuitry.
2. Instruments of conventional resolution and/or sensitivity can be constructed at a reduced cost.

[*Price 25p*]

3. Alternatively, instruments of higher resolutions and/or sensitivities can be constructed at the same cost.

The broadest aspects of the present invention may be understood by considering the differences between the particular and relevant versions of the Hill equation, i.e. $\ddot{x}+g(t)x=f(t)$ and the Mathieu equation i.e. $\ddot{x}+(a+b)\cos w\,t)x=f(t)$. In these equations, x represents the distance travelled by an ion from its source, and t the time taken to travel that distance; a and b are constant. It is inherent in the specification that the time-varying function g(t) be periodic or very nearly so, for example quasiperiodic or slowly swept periodic.

Either the magnitude of the time-varying voltage g(t) or its frequency can be varied (i.e. swept) at a relatively slow rate so that the mass-response of the mass spectrometer is scanned over a desired mass range or ranges.

The Mathieu equation is a special case of the Hill equation where g(t) is allowed to be a constant plus a sinusoid and this would include the case where the constant was zero. The actual operation of mass spectrometers of the quadrupole type constructed and used to the present day is described by this equation, following the disclosure in United States of America Patent Specifications Nos. 2,939,952 and 2,950,389. In these, the constant portion of the function g(t) is related to a D.C. or constant potential applied to the analysing electrodes of the mass spectrometers whilst the sinusoid is related to a high frequency sinusoidal potential generated separately from and applied to such electrodes together with said D.C. potential. At the times of filing of the said Patent Specifications Nos. 2,939,952 and 2,950,389 a sinusoidal potential would have been the most easily generated high frequency periodic waveform. An important limitation on the quality of measurements made with this mode of operation results from the need to maintain the ratio of the magnitude of the sinusoidal potential to the magnitude of the constant potential constant to tolerances which approach the limit even of present day electronic technology. This limitation also applies when the sinusoidal potential is replaced by any other periodic waveshape. The present invention does not include such a mode of operation where a constant potential is applied to the analysing electrodes of a mass spectrometer of the quadrupole type together with a high frequency periodic potential. Instead only one waveform is applied to the analysing electrodes of such device being a waveform which contains its own constant component intrinsically by reason of the method by which it is generated. An example of such a waveform and such a means for generation would be a rectangular waveform generated by an electronic switching circuit, where the repetition rate and duty cycle of the rectangular waveform can be controlled simply by controlling the operation of the switching circuit. Duty cycle is taken to mean the time interval over which the rectangular waveform is at its most positive potential divided by the period of the waveform. In the present invention therefore a D.C. or constant potential is not generated separately to the high frequency periodic potential and thus not applied together with the high frequency potential to the analysing electrodes of a mass spectrometer of the quadrupole type, as it is and has been for devices operated according to the disclosures in the said Patent Specifications Nos. 2,939,952 and 2,950,389.

The requirement on the waveform to be used according to the present invention are that it be periodic and contain an intrinsic constant component which may be varied by changing a parameter of the waveform, such as the duty cycle in the example cited above. The actual shape of the waveform over one period is not important. This may be confirmed by noting that if the waveform is expanded in a Fourier series it may be shown that only the first three or four harmonics have any significant effect on the operation of mass spectrometers of the quadrupole type.

The time-varying function describing the electric potential applied to the electrodes of a mass spectrometer of the quadrupole type may be formed by a repetitive sequence of segments each one of which is composed of either one or a number of linearly-varying functions of time and/or one or a number of exponentially-varying functions of time where the exponents of each portion are either real functions of time or complex functions of time but not purely imaginary functions of time.

According to the present invention there is provided a mass spectrometer of the quadrupole type as herein defined, comprising means for generating a single periodic or quasi-periodic time varying electrical potential which incorporates a zeroth harmonic term in its Fourier expansion, the zeroth harmonic term being generated simultaneously with the other components and not separately generated and added to the other components, and applying said potential to the analyzing electrodes of the mass spectrometer, the waveform of said potential being formed by a repetitive sequence of segments each one of which is composed of at least one substantially linearly-varying function of time and/or at least one substantially exponentially varying function of time where the exponents of each portion are either real functions of time or complex functions of time but not purely imaginary functions of time.

The definition of the function g(t) according to the invention thus excludes the case where g(t) is either a sinusoid or very nearly a sinusoid due to unavoidable deficiencies in the construction of electrical sinusoidal oscillators in the present state of the art where the harmonic content, although reasonably small, cannot be entirely reduced to zero.

The mathematical technique known as Fourier Analysis may be used with some particular examples to assist in the explanation of the present invention. Fourier analysis states that any periodic waveform g(t) may be represented as a series of weighted sinusoidal terms with frequencies nf where f is the frequency corresponding to the period with which the waveform is repetitive and n is an integer which can take on the successive values from zero to infinity. For most practical purposes instead of proceeding to an infinite number of terms the Fourier series may be truncated at a term where n is a suitably chosen finite number taken not too large, and it is known that the error generated by performing this truncation will not be greater than the magnitude of the next succeeding term.

The frequencies of individual terms are thus commensurate i.e. can be expressed exactly by the ratio of two integers. In addition the phase angles to be attributed to each term will be coherent i.e. in some fixed relationship to each other due to the fact that the waveform is the output from a single generating source. In addition the weights i.e. coefficients attached to each term will bear to each other constant ratios which are determined solely by the shape of the waveform g(t).

A waveform which is exactly sinusoidal will have only one non-zero coefficient in its Fourier series expansion, i.e. the coefficient corresponding to the value n=1. Practically realizable sinusoidal oscillators generate harmonic terms i.e. frequencies with n=2, 3 . . . etc. with small amplitudes and the output from such oscillators when provided by the conventional means of inductive and/or capacitive coupling will contain no D.C. term or zeroth harmonic term, i.e. the coefficient corresponding to the value n=0 will be zero.

On the other hand a periodic waveform which is rectangular or trapezoidal or substantially so in shape and which is arranged to possess equal and fixed or very nearly equal and fixed values of peak electric potential with respect to the earth or electric potential-reference node of its electric circuit will possess a Fourier series expansion with substantially non-zero coefficients for many terms including particularly n=0, 1, and higher integers. Using the notation A_n to indicate the value of the coefficient in the term where the said integer is equal to n, each of the ratios An/Ao where n takes the values 1, . . . and higher integers will be fixed exactly and precisely by the shape of the waveform.

In the case of a waveform comprising a D.C. component and a single sinusoidal component provided from separate sources the ratio A1/Ao will be determined by the characteristics including the stability of each of the two generating sources.

In the case of a waveform comprising a D.C. component and a hierarchy of sinusoidal harmonics provided from a single source the ratio A1/Ao and also the ratios An/Ao where n=2 and higher integers will be determined solely by the shape of the waveform.

Such waveforms as are pertinent to the present invention may be generated by the sequential summation in time of a convenient and practicably small number of successive segments or portions which are either linearly or exponentially (with real or complex but not purely imaginary argument of the exponential) time-varying potentials or a summation of such linear and/or exponential components. In this connection it is to be noted that two or ten such successive segments or components is recognisably a practical and practicably small number of components whereas two hundred or one thousand such successive segments or components are not.

Certain waveforms for the function g(t), such as, but not restricted to, rectangular periodic or trapezoidal periodic (or quasi-periodic) or practically realizable approximations to these idealized waveforms are especially advantageous for the purposes of improving the performance and/or reducing the cost of mass spectrometers of the quadrupole type. These advantages are realizable compared to the equivalent mass spectrometers and mass filters whose electrodes are excited by constant electrical potentials or sinusoidal potentials generated at discrete non-commensurate frequencies or combinations of such constant and sinusoidal potentials.

The invention is illustrated by way of example in the accompanying diagrammatic drawings in which:—

Fig. 1 is a diagram illustrating the mechanical arrangements of the parts of a quadrupole mass filter or spectrometer,

Fig. 2 is a diagram showing the system used to energize the electrode in a conventional Paul-Mathieu type of mass spectrometer,

Fig. 3a illustrates the waveform used in a Paul-Mathieu type of mass spectrometer in which the potential applied to the electrodes is a combination of a dc potential and a sinusoidally varying potential,

Fig. 3b illustrates a rectangular waveform used according to the present invention,

Fig. 3c illustrates a trapezoidal waveform

used according to the present invention having a similar duty cycle,

Fig. 4 is a block diagram of means for energising the electrodes of a mass spectrometer with a time-varying potential according to the invention,

Fig. 5 is a block diagram of a further means for energising the electrodes of a mass spectrometer according to the invention,

Fig. 6 is a diagram illustrating the mechanical arrangement of the parts of a quadrupole mass filter or spectrometer in which auxiliary electrodes are arranged adjacent the main electrodes, and

Figs. 7a to 7d are diagrams showing various alternative forms of electrical coupling between the main and auxiliary electrodes.

In Figure 1 is shown an electrode system of similar type to that used in a conventional Paul-Mathieu quadrupole mass spectrometer which is set up in a suitably evacuated chamber 10 provided with an ion source 11 into which may be introduced small quantities of the sample, compound or element under investigation. The quadrupole filter consists of four parallel metal electrodes 12, each approximating an electrically conducting cylindrical hyperboloid placed symmetrically about the device so that the necessary spatially-linear electrical field is closely realized. This filter is followed by an ion detector 13, which may be, in the present state of the art, either a Faraday cup or an electron multiplier, but which in the future state of the art might alternatively be an active electronic or quantum electronic device and which is employed, together with a suitable recording or display unit, to register the absolute or relative number of focussed ions which have been passed through the mass filter.

Fig. 2 shows the conventional arrangement for energising the electrodes of a mass filter or spectrometer as shown in Fig. 1. This consists of a sinusoidal oscillator source 14, a regulated D.C. source 15, a means 16 to add these voltages connected to the electrodes of a mass filter 17. Fig. 3a shows the waveform of the sinusoidal voltage and the waveform produced by combining them.

Fig. 3b and Fig. 3c show respectively a rectangular and trapezoidal waveform which are two preferred waveforms for use in accordance with the present invention for energising the electrodes of a mass filter or spectrometer. The duty cycle in the case of these two waveforms may be expressed as

$$\frac{\tau}{T}$$

or

$$\frac{T-\tau}{T}.$$

In Figures 4 and 5 are shown in simple block diagram form, arrangements for achieving the energisation of the electrodes of a Hill-equation type mass spectrometer of the quadrupole type by electrical potentials as described elsewhere in this document which may be generated by a variety of means. The means indicated in the diagrams Figure 4 and Figure 5 exclude the necessity for a sinusoidal or quasi-sinusoidal electrical generator except for the likelihood that such a generator might be used as the initial reference within the periodic clock source. The various integers of these arrangements are named on the figures. They are all conventional pieces of apparatus the nature and functioning of which is well known to those skilled in the art and they will not therefore be described in detail.

The means shown in Figure 4 enables the generation of a nearly rectangular or nearly trapezoidal waveform whose duty cycle or mark-space ratio may be readily varied by manipulating the value of the adjustable time delay shown. It is a further advantage of the invention that the added D.C. source as shown for example in Figure 5 may be dispensed with and that if it is employed the ratio of the added D.C. potential to the alternating potential as used in the Mathieu-equation type mass spectrometers and filters does not have to be controlled very precisely as the major means of mass selection. In the example shown in Figure 4 it will be evident that the D.C. component of the waveform applied to the electrodes is inherent in the single waveform produced by the generator and that the magnitude of this D.C. component may be controlled with great precision by the adjustable time delay as shown in the diagram Figure 4. It is well known in the electronics art that timing of digital impulses may be controlled with great accuracy. On the other hand the control of the ratio of an alternating to a direct voltage as is required in the conventional Mathieu-equation type of mass spectrometer or mass filter cannot be achieved with such great accuracy nor with such inexpensive arrangements.

The use of a variable time delay although convenient in some cases is not essential to the generation of a waveform in which the amount of the D.C. component of the time-varying waveform may be controlled so as to enable effective operation of a mass spectrometer or mass filter. For example in the arrangement shown in Figure 5 the added D.C. source may be eliminated and the D.C. component controlled entirely by the shape and amplitudes of the waveform components which may be switched at either fixed or variable times relative to the clock pulses provided by the periodic sources. Such means for switching at times either variable or fixed in relation to the pulses at clock frequency or at an integral multiple or sub-multiple of the clock

frequency are well known in the electronics art.

It may also be advantageous in the present state of the art to incorporate auxiliary analyzing electrodes in order to influence ion trajectories particularly near the entry to the main electrodes. Such influence may be thought of either as pre-focussing or as pre-filtering in order to improve the sensitivity and/or resolution of the spectrometer. This artifice may also be employed profitably with the class of waveforms pertinent to the present invention. In Figure 6 is shown an arrangement wherein the main electrodes 18 of a quadrupole mass spectrometer are energized at points X_1 X_2 Y_1 Y_2 by the waveforms described earlier in this specification and in which a D.C. and higher frequency components are present in the Fourier series expansion of the waveform. Shown also in this figure are auxiliary analyzing electrodes 19 in a co-axial quadrupole disposition, with a simple capacitive coupling 20 to each main electrode. This coupling would remove the D.C. component from the waveform applied to the auxiliary analyzing electrodes. Alternative coupling arrangements are shown in Figures 7a to 7d whereby the D.C. component may be removed or modified as is most advantageous for the various desirable purposes of pre-focussing and/or pre-filtering the ions admitted to the main electrodes of the mass spectrometer. In each case the left hand side of the coupling is connected to a main electrode and the right hand side to an auxiliary analyzing electrode. In the case of the couplings shown in Figs. 7a and 7b the ratio of the magnitude of the D.C. component of the waveform applied to the auxiliary analyzing electrode to the magnitude of the other components is made zero. In the case of the coupling of Fig. 7c the ratio may be reduced and in that of Fig. 7d either increased or reduced depending in the circuit parameters.

A consideration of the effects of applying a rectangular R.F. waveform to the electrodes of a quadrupole mass spectrometer is set out in a paper by the present inventors entitled "On the time varying potential in the quadrupole mass spectrometer" published in the Proceeding of the Institution of Radio and Electronics Engineers Australia, August 1971 on page 321.

WHAT WE CLAIM IS:—

1. A mass spectrometer of the quadrupole type, as herein defined, comprising means for generating a single periodic or quasi-periodic time varying electrical potential which incorporates a zeroth harmonic term in its Fourier expansion, the zeroth harmonic term being generated simultaneously with the other components and not separately generated and added to the other components, and applying said potential to the analyzing electrodes of the mass spectrometer, the waveform of said potential being formed by a repetitive sequence of segments each one of which is composed of at least one substantially linearly-varying function of time and/or at least one substantially exponentially varying function of time where the exponents of each portion are either real functions of time or complex functions of time but not purely imaginary functions of time.

2. A mass spectrometer as claimed in Claim 1, wherein the waveform is substantially rectangular in character and the said means includes means for varying the duty cycle of the waveform.

3. A mass spectrometer as claimed in Claim 1, wherein the waveform is substantially trapeezooidal in character and the said means include means for varying the duty cycle of the waveform.

4. A mass spectrometer as claimed in any preceding claim, wherein the said first mentioned means incorporates means for varying the ratio of the amplitude of the zeroth harmonic term and the other terms in the Fourier series.

5. A quadrupole mass spectrometer as claimed in any preceding claim and comprising auxiliary analyzing electrodes, wherein the said first mentioned means incorporates means for energising the said auxiliary analyzing electrodes with a potential the waveform of which is different from the waveform of the potential applied to the analyzing electrodes.

6. A mass spectrometer as claimed in any preceding claim wherein said first mentioned means incorporates means whereby operating values of said waveform are varied in time at a relatively slow rate so that the mass response of the mass spectrometer is scanned over a desired mass range or ranges.

7. A mass spectrometer substantially as described herein with reference to Figures 3 to 7 of the accompanying drawings.

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1346393 COMPLETE SPECIFICATION
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

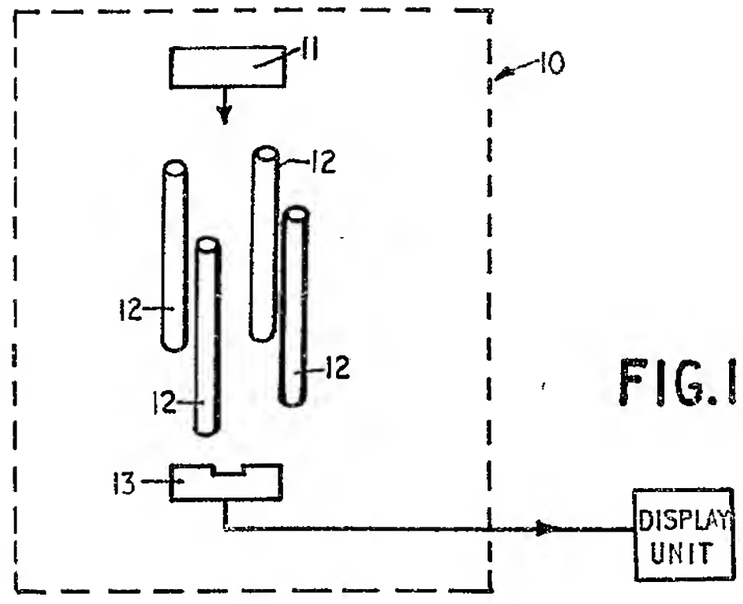

FIG.1

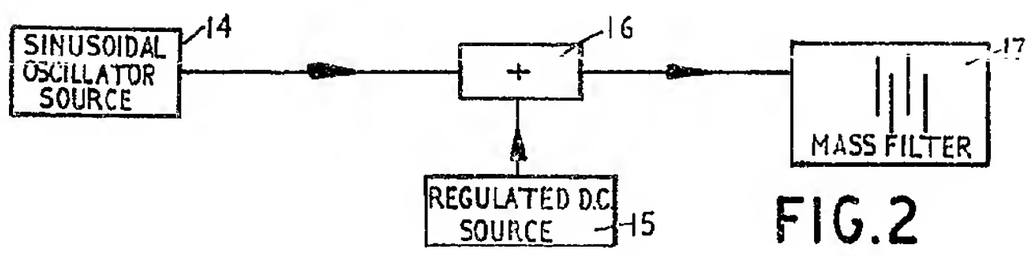

FIG.2

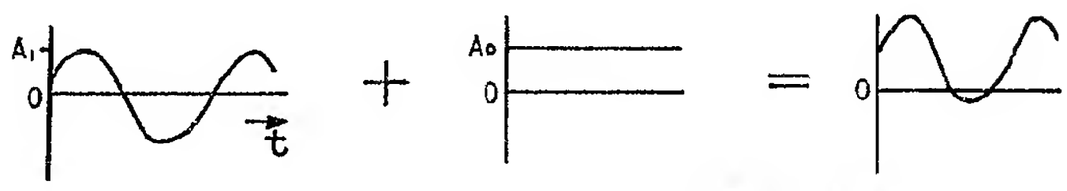

FIG.3a

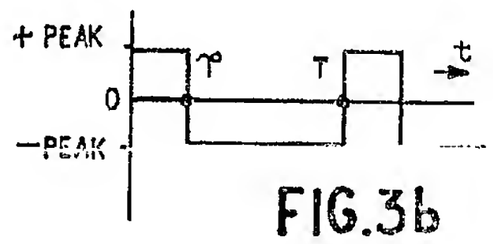

FIG.3b

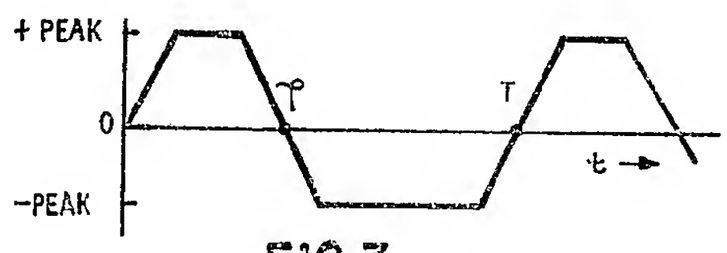

FIG.3c

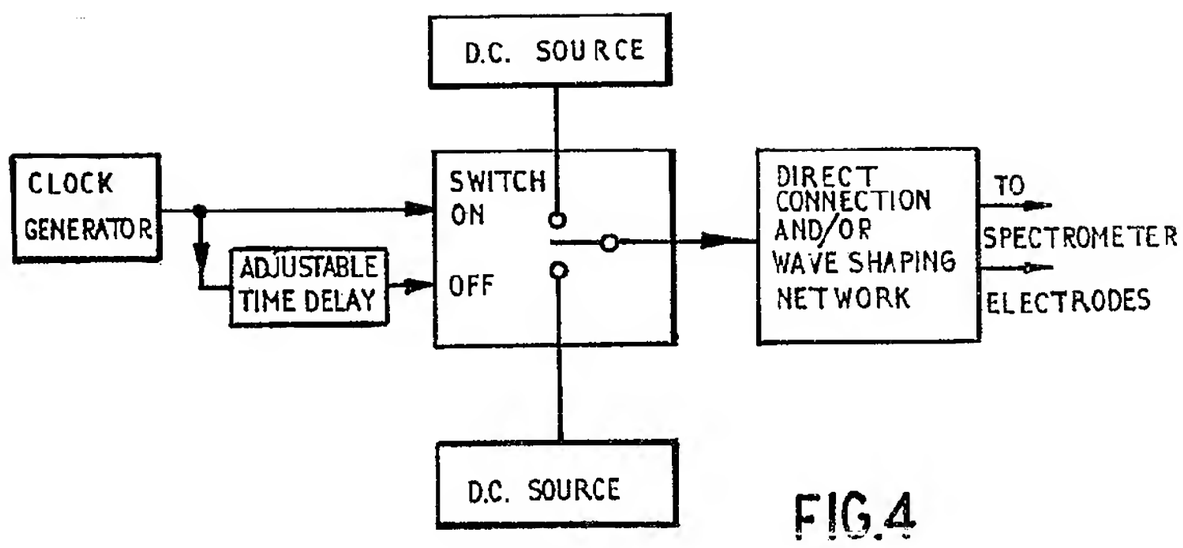
D.C. SOURCE
CLOCK GENERATOR
ADJUSTABLE TIME DELAY
SWITCH ON
OFF
DIRECT CONNECTION AND/OR WAVE SHAPING NETWORK
TO SPECTROMETER
ELECTRODES
D.C. SOURCE

FIG.4

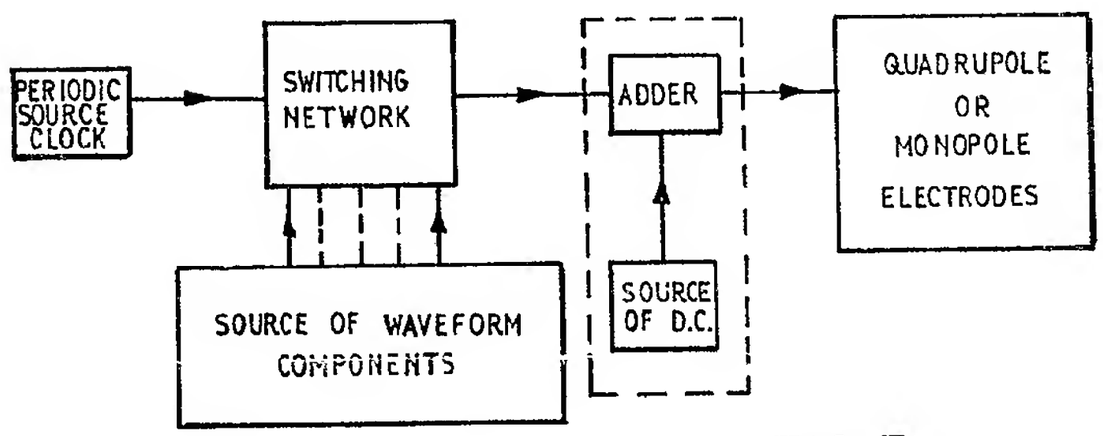
PERIODIC SOURCE CLOCK
SWITCHING NETWORK
ADDER
QUADRUPOLE OR MONOPOLE ELECTRODES
SOURCE OF WAVEFORM COMPONENTS
SOURCE OF D.C.

FIG.5

1346393 COMPLETE SPECIFICATION
3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 3

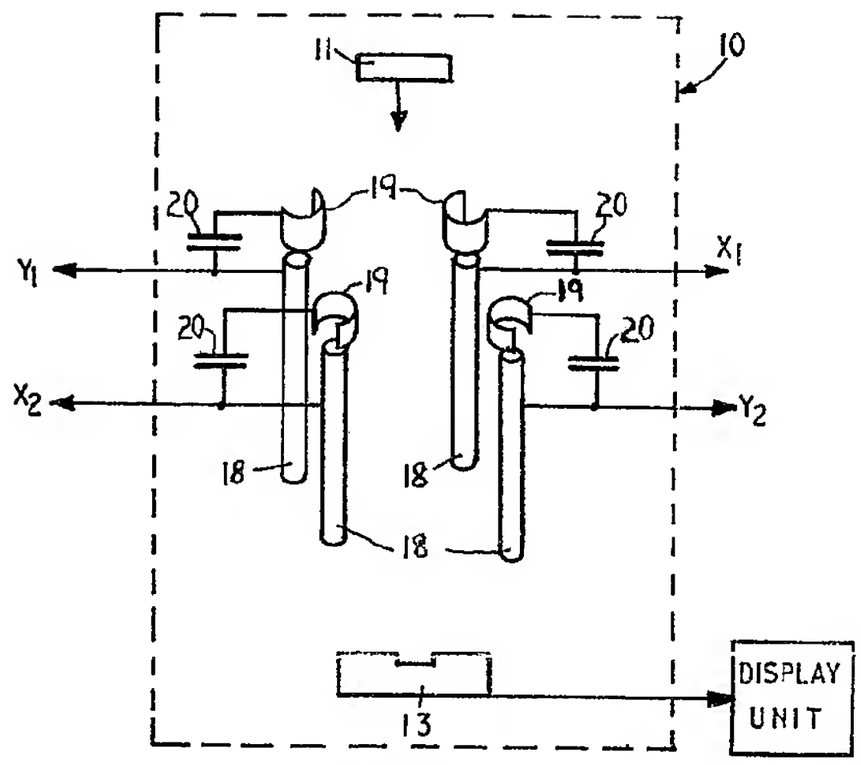

FIG.6

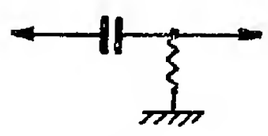

FIG.7a

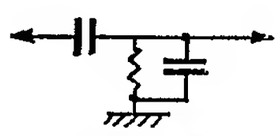

FIG.7b

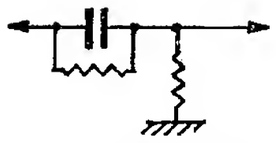

FIG.7c

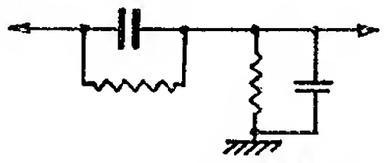

FIG.7d